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Novel Approach for Sandstone Acidizing Using in Situ-Generated Hydrofluoric Acid with the Aid of Thermochemicals

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ABSTRACT: In this study, an in situ-generated hydrofluoric acid (HF) was used for sandstone acidizing, where an acid precursor (ammonium fluoride NH_4F) reacted with a suitable oxidizer (sodium bromates $NaBrO_3$) in an exothermic reaction. First, the new chemical mixture was prepared to react with pure quartz samples and the reaction effluent was analyzed to identify the presence of Si^+ ions using the inductively coupled plasma (ICP) technique. Core flooding experiments were performed using Gray Berea sandstone cores (6 in. length and 1.5 in. diameter). A preflush stage of 5 PV of 7 wt % HCl was injected to remove any calcite content in the core. The main chemicals were then flushed for 3 successive cycles of 1 PV each. To assure core integrity, scratch tests and NMR scans were run on the core sample before and after the treatment. The new chemical mixture could dissolve the quartz sample and reduce its weight by 80 mg. The concentration of the dissolved Si^+ ions was more than 90 ppm. This proves the capability of the chemical mixture to generate HF. The initial core permeability was measured at a stabilized flow rate of 2 cm^3/min to be 33 mD. After the acid preflush stage, the core permeability reduced to 31 mD. Core permeability increased immediately after the first treatment cycle and reached 41 mD. At the end, the core flooding results showed a permeability improvement for Gray Berea sandstone cores by almost 40%. The ICP analysis of the effluent showed a total amount of chelated Si^+ ions of about 10.5 mg. In addition to the high temperature generated in the near-wellbore area, the pressure increased because of the produced nitrogen gas from the exothermic reaction and reached about 600 psi. The scratch test showed an increase in the sample uniaxial compressive strength from 7432 to 9235 psi. The dynamic Poisson's ratio and the dynamic Young's modulus increased as well from 0.17 to 0.19 and from 2159 to 3585 ksi, respectively. The enhancement in the mechanical properties of the core can be attributed to the presence of the potassium element in Berea cores and its solidification reaction with the HF generated. The NMR measurements of the core sample before and after the acidizing process show an increase in the core porosity; however, the core preserved its original pore system. Upon application of this new stimulation technology, the true production potential of sandstone reservoirs can be achieved, well tubular corrosion will be minimized, and handling hazardous chemicals such as HF will be avoided. Most importantly, controlling the reaction rate, by controlling the amount of exothermic chemicals, can ensure deep acid penetration as well.
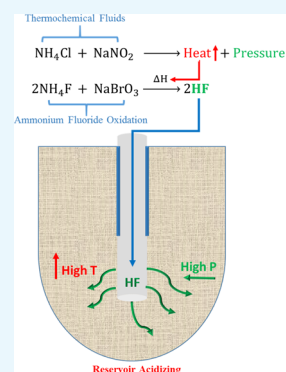
1. INTRODUCTION

The term "formation damage" refers to the decrease in the formation permeability by different improper activities. Operationally and economically, formation damage is considered an undesirable problem that is expected to take place at any stage of the reservoir life.[1] As expressed by Amaerule et al.,[2] "formation damage is an expensive headache to the oil and gas industry". Bennion[3] described formation damage as, "the impairment of the invisible, by the inevitable and uncontrollable, resulting in an indeterminate reduction of the unquantifiable!"

Formation acidizing and hydraulic fracturing are both two common solutions to mitigate the formation damage problem. The hydraulic fracturing process aims to bypass the damaged zone around the wellbore by creating a high permeability path within the reservoir that is connected to the well.[4−6] On the other hand, acidizing treatment aims generally to enhance the well productivity by either dissolving the formation rock itself

or removing the well-induced damage.[7−11] Acid treatment was initially used to stimulate carbonate reservoirs by dissolving the rock matrix.[12] However, with the industry development, special types of acid were evolved to treat sandstone reservoir damage that occurs during drilling, completion, enhanced oil recovery, or even production period.[13,14]

Sandstone matrix acidizing, where the acid is injected at a pressure lower than the formation fracture pressure and reacts near the wellbore area, can reach as deep as only 1 ft.[15] The main goal of sandstone acidizing is not to influence a large deep portion of the reservoir but to highly improve or restore the near-wellbore permeability.[16] Sandstone formations are

therefore commonly stimulated using hydrofluoric acid (HF)-based systems, which may also be blended with strong mineral acids, organic acids, esters, and combinations thereof.[17−19]

The process of sandstone acidizing with mud acid is quite challenging as it comprises various stages containing different fluids. Some precipitation reactions could take place during any stage of sandstone acidizing. This may harm the stimulated formation and reduce its permeability and porosity.[12,20] The sandstone acidizing process comes in three main phases.[21,22] The first stage is called a "preflush" in which the main purpose is to dissolve the formation carbonates and evict the inhabitant saline water. The second stage or the mud acid stage comprises mainly injection of HCl and HF acids with prestated concentrations. The main purpose of this stage is to get rid of all the near-wellbore materials that thought to be restricting the production such as clays and feldspars. Finally, the "after flush" stage which aims at pushing the mud acid stage further into the reservoir and wash out the byproducts resulted from the previous reactions. The chemicals used in this final stage can vary between hydrochloric acid (HCl), ammonium chloride (NH_4Cl), or even a pure hydrocarbon solvent such as diesel oil.

The reaction of mud acid with sandstone formations is a fast reaction, and the acid is spent quickly before reaching the proper depth.[23] Fines migration would probably occur after mud acid treatment and restore the formation damage. The reaction of HF with silicate minerals produces fluosilicic acid that reacts with the different cations present in the formation and produces precipitates such as $CaSiF_6$, Na_2SiF_6, and K_2SiF_6.[24−26] In addition to the reservoir problems caused using conventional HF, surface handling of the stimulating chemicals is very risky to the working crew and to the equipment. Both HF and HCl are highly corrosive and require high safety precautions to deal with.[27]

The first trial of sandstone formation acidizing using a mixture of HCl and HF was run by Halliburton in 1933 in Texas. Unexpectedly, the results were disappointing and discouraging. After that, in 1939, a mixture of 12% HCl−3% HF was introduced under the name of "mud acid" or "regular strength mud acid" and it gave promising results once pumped downhole.[28] Because silica is the main mineral constituent of sandstone, its reaction with HF at low temperatures occurs at a low rate.[29] On the other hand, aluminosilicates such as clays and feldspars react rapidly with mud acid throughout a three-stage reaction to produce some insoluble precipitates as shown in the following reaction equations (eqs 1−3).[30−32]

The primary reaction

$$\text{aluminosilicates} + HF \rightarrow H_2SiF_6 + 2H_2O \tag{1}$$
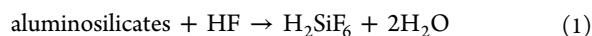
Then the produced fluosilicic acid reacts with different aluminosilicates such as potassium feldspars throughout a secondary reaction as follows

the secondary reaction

$$SiF_6{}^{2-} + 6KAlSi_8O_8 + 20H^+ + 10H_2O$$
$$\rightarrow 6K^+ + 6AlF^{2+} + 18H_2SiO_3 + H_4SiO_4 \tag{2}$$
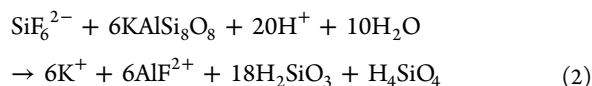
After that, the ratio of fluorine (F)/aluminum (Al) continues to decrease in the aluminum fluoride compounds because of their reaction with aluminosilicate compounds in the presence of HCl. This reaction chelates the aluminum ions

from the aluminosilicates leaving silica gel as a precipitate as following

The tertiary reaction

$$AlF_2{}^+ + KAlSi_3O_8 + 4H^+ + 4H_2O \rightarrow K^+ + 2AlF^{2+}$$
$$+ 3H_4SiO_4 \tag{3}$$
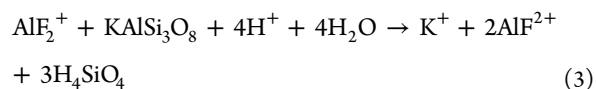
The previous three stages of the reaction of sandstone rock minerals with conventional mud acid take place along the offset distance from the well into the reservoir (Figure 1). The

Figure 1. Three stages of the reaction of mud acid with the sandstone matrix.

primary stage is near the wellbore where the aluminum and silica fluorides are produced. The secondary stage is where the primary products go under slow reaction to form silica gel which preprecipitates in the reservoir. Further away from the well, a tertiary reaction takes place where more precipitating silica gel is produced. This gives an indication of the failure potential of the sandstone stimulation process with the conventional mud acid method.

To solve the problems associated with stimulating sandstone formations using conventional mud acids, some trials were made to find more appropriate alternatives for mud acid. Templeton et al.[33] proposed the approach of self-generating in situ HF. Templeton et al. used a water-soluble fluoride salt (e.g., ammonium fluoride) along with an organic acid ester (e.g., methyl formate) in order to generate HF as described by eqs 4 and 5. However, this method suffers from two main issues. First, organic esters are highly flammable. Second, temporary damage can occur during the reaction of HF with the formation clays, which forms some insoluble products such as ralstonite.[34]

$$HCOOCH_3 + H_2O \rightarrow HCOOH + CH_3OH \tag{4}$$

$$HCOOH + NH_4F \rightarrow NH_4{}^+ + HCOO^- + HF \tag{5}$$
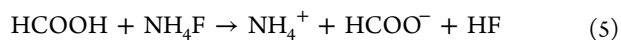
In order to overcome the problem of the quick reaction and consumption of conventional mud acid, Gdanski[35] and Ayorinde et al.[36] adopted the use of some retarded acids such as fluoroboric acid (HBF_4) and fluroaluminic and hexa-fluoro-phosphonic (HPF_6) acids. The use of these weak acids aims at increasing the depth of penetration of the acid treatment by generating HF at a slower rate. The preliminary results of this approach are better than the use of conventional mud acid. However, the acid depth of penetration was not highly increased and the formation consolidation problem

along with the unwanted precipitation of HF reactions with sandstone minerals are not retarded that much.[27]

Rogers et al.[37] proposed the formulation consisting of 10% citric acid along with 1.5% HF without any further additives for stimulating sandstone formations containing the zeolite mineral. The proposed formulation showed an effective dissolution to the zeolite particles without creating silica gel precipitation. This could prevent the postdamage problem caused by conventional mud acid treatment. However, the used HF did not penetrate deep into the formation and reacted only with the shallow damage and scale deposits around the wellbore.[34] Al-Dahlan et al.[29] used the phosphonic acid-based retarded HF (PRHF) system to stimulate sandstone formations. The results show that the PRHF could not extract the calcium (Ca) and magnesium (Mg) ions from the clay minerals.

Mahmoud et al.[26] used 20 wt % GLDA (glutamic acid-N, N-diacetic acid) combined with 1 wt % HF to stimulate different sandstone cores. Computed tomography scans showed a reduction in the CT number values because of precipitation of CaF_2. Al-Harbi et al.[38] used solutions of ethylenediaminetetra-acetic acid (EDTA) containing ammonium bi-fluoride with sandstone cores. The amount of AlF_3 precipitated was a strong function of the Al/F ratio in the solution. Li et al.[39] introduced a new acid system that consists of a combination of chelating agents, phosphoric acid (H_3PO_4), and NH_4F for high-temperature applications for sandstone reservoirs. The new acid system has a low corrosion rate and prevented the precipitation of CaF_2.

Karale et al.[40] used a pH buffer solution to activate an exothermic reaction downhole. They used sodium nitrite and ammonium chloride as the main reactants for their exothermic reactions. One of the reactants can be injected to the formation first or both can go together, and then, a pH buffer solution with the pH value less than 4 is injected to activate the exothermic reaction described by eq 6. The generated heat increases the formation temperature and in turn increases the acid reaction rate. This method was initially developed for increasing the efficiency of acidizing low-temperature dolomite formations. Al-Nakhli et al.[41] proposed the use of thermochemical reaction as a novel cost-effective method for heavy oil recovery. This new approach is called the ExoClean technique that provides in situ steam generation for thermal recovery of deep oil wells. They reported the increase in system pressure and temperature to be 3470 psi and 600 °F, respectively, after the reaction is completed.

$$NH_4Cl + NaNO_2 \rightarrow NaCl + 2H_2O + N_2 + \Delta H \text{ (heat)} \tag{6}$$
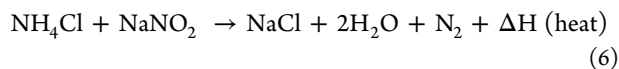
Alade et al.[42] used the concept of thermochemical reactions for enhancing the production of heavy oil and condensate reservoirs. They evaluated the kinetics and energy associated with the thermochemical reaction and concluded that the initial temperature highly affects the reaction rate. The reaction duration decreased from almost 18 min under the ambient temperature of 20 °C to about 6 min under 75 °C. Moreover, the change in enthalpy ΔH for this chemical reaction was 369 kJ mol^{-1}, regardless of the operating temperatures.

A recently adopted technique for generating HF involves the oxidation of ammonium fluoride salt with a strong oxidizer. This oxidation reaction is an autocatalytic reaction that requires heat to initiate. Hull et al.[43] used sodium bromates ($NaBrO_3$) as a powerful oxidizer to react with ammonium

fluoride and produce HF according to eq 7. This reaction requires heating the reaction medium up to 150 °C for 3 h in order to produce a transparent solution.

$$2NH_4F + NaBrO_3 + \Delta H \text{ (heat)}$$
$$\rightarrow 2HF + NaBr + 3H_2O + N_2 \tag{7}$$
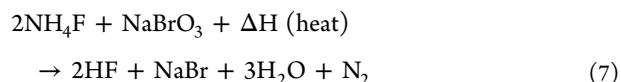
The main objectives of this work are to overcome the drawbacks of conventional mud acid treatment by adopting a novel approach of generating an in situ HF system. This is accomplished by combining what Hull et al.[43] and Karale et al.[40] did together. In other words, this research aims at combining the application of thermochemical reaction that can generate heat up to 200 °F with the application of oxidizing ammonium fluoride salt under high temperature in order to generate in situ HF. Combing the two mentioned concepts together would help in generating the heat required for the endothermic oxidation reaction of ammonium fluoride, producing a high-pressure pulse that is capable of removing any byproduct precipitation. Nitrogen gas is also expected to be produced which would be of a good benefit for diverting the acid solution during the acidizing treatment. The generated acid will be used to remove the damage from the sandstone formations, while the generated pressure pulse provided enough energy to flow back the well and create some microfractures.

In order to achieve the objectives of this work, all the required materials were first prepared, including the thermochemical fluids, the acid-generating fluids, pure quartz samples, and sandstone core samples. The general methodology followed was to ensure the validity of the proposed concept by carrying out different tests and measurements such as the quartz solubility test, core flooding experiments, inductively coupled plasma (ICP) analysis, NMR scans, and finally scratch tests. These tests evaluate different chemical, petrophysical, and mechanical parameters of the used chemicals and rock samples.

2. RESULTS AND DISCUSSION

The initial results of adding the in situ acid-generating fluids and the thermochemicals to the aging cell along with the quartz samples for 24 h at a temperature of 90 °C showed a change in the quartz sample weight from 3.4040 to 3.3235 g with some notches on the surface of the quartz sample (Figure 2a,b). This reduction in the quartz weight by 80.5 mg proved the formation of HF that can dissolve the silicate minerals and reduce the quartz weight. Moreover, these notches observed on the sample surface indicate the active reaction zone between the generated HF and the silica mineral. The ICP results of the experiment final solution showed a silicon ion (Si^+) concentration of 91.43 ppm. The heat is not only the desirable product out of the exothermic reaction. Nitrogen gas (N_2) also evolves and increases the system pressure by 600 psi.

The Gray Berea sandstone core and the saturating fluid properties are listed in Table 1. The elemental composition of the Gray Berea sandstone cores using the X-ray fluorescence (XRF) analysis is listed in Table 2, while the mineralogy analysis of the core is shown in Figure 3. As expected, Si and O_2 represent the most abundant elements in the Berea rock sample. This is reflected by the high quartz content that the core possesses which reaches up to 87%. The core is also distinguished by the high potassium content present in the potassium feldspars. Because the dry weight of the Berea core

Figure 2. (a) Quartz sample before the reactions with a weight of 3.404 g with sharp edges and a clear surface. (b) Quartz sample after chemical reactions with a weight of 3.3235 g with notches on the surface because of HF generated.

Table 1. Berea Sandstone Core Properties with the Saturating Fluid Properties

dry weight (g)	356.6
saturated weight (g)	389.8
diameter (in.)	1.496
core length (in.)	5.856
fluid salinity	3 wt % KCl
fluid density (g/cc)	1.0166
core bulk volume (cc)	168.68
core pore volume (cc)	33.75
porosity	0.2

Table 2. Elemental Composition of the Gray Berea Sandstone Cores Using XRF Results

element	wt %
O	51.52
Si	40.4
Al	4.18
K	1.51
Fe	0.76
Mg	0.35
Ti	0.35
Na	0.33
Ca	0.29
Cl	0.14
Zr	0.06
S	0.04
Cr	0.03
P	0.03
Mn	0.02
sum	100

is about 356.6 g, it must contain an amount of quartz that weighs about 310 g.

The initial core permeability was measured using the 3 wt % KCl solution. At a stabilized flow rate of 2 cm^3/min, the core permeability was calculated to be 33 mD. Flushing the core with 5 PV HCl, having a concentration of 7 wt %, led to a decrease in the core permeability to 31 mD (the core lost about 4.8% of its original permeability). This can be attributed to the reaction of HCl with the clay minerals (chlorite, illite,

and kaolinite) existing in the core. This matches with the observations of Thomas et al.[44] and Kamal et al.[45] about the effect of HCl acid on the clay-containing rocks. HCl reacts with chlorite to produce ferric hydroxide which is a gel material that can plug the pore throats. Also, HCl reacts with both illite and kaolinite and causes fines migration. The main treatment started by injecting 0.5 PV of the acid-generating solutions (ammonium fluoride and sodium bromates) followed by 0.5 PV of the exothermic chemicals (ammonium chloride and sodium nitrite). The system temperature is then increased to 90 °C to initiate the exothermic reaction. The inlet and outlet valves of the core are then closed, and the first soaking period of about 30 min was performed. The core inlet pressure started to increase, indicating the start of the exothermic reaction. The maximum reached inlet pressure during this stage was about 611 psi. The same flushing and soaking procedures were followed during the second and third cycles. The increase in the inlet pressure during the second and third cycles was 456 and 424, respectively. The inlet pressure profile corresponding to each flooding stage is shown in Figure 4.

Core permeability has increased immediately after the first treatment cycle and reached 41 mD. After the second cycle, the permeability increased more and reached about 44 mD. No noticeable change in the core permeability was found after the third treatment cycle. Finally, the core is flushed by 3 wt % KCl from the reverse direction (backflow) and the final permeability was measured. The final permeability measurement showed an enhancement in the core permeability by about 40%. All the effluents were collected for ICP-optical emission spectrometry (OES) analysis to determine the total amount of the dissolved Si$^+$ ions. The permeability measurement after each flooding stage is shown in Figure 5.

The ICP-OES results showed the presence of Si$^+$ ions in each effluent after each treatment stage. This again proves the generation of HF inside the Berea sandstone core. Figure 6 shows the cumulative amount of the chelated Si$^+$ ions from the core after each treatment cycle. There is a gradual increase in the cumulative amount of the chelated Si$^+$ ions after the first two cycles. However, there was a sharp increase in the amount of the Si$^+$ ions chelated from the core after the third cycle. This is also clear from analyzing the effluent from the after flush stage. The reason behind this is the maturity of the reaction after the first two cycles and the ability of the injected chemical to be exposed to a larger area of the rock. The total chelated amount of Si$^+$ ions from the core reached 10.5 mg. This is corresponding to a total dissolved amount of 22.5 mg of quartz (silica). This could be the reason behind the permeability enhancement of the Gray Berea sandstone core after this treatment process.

NMR measurements for the Gray Berea core before and after the treatment showed an increase in the core final porosity. This is attributed to the amount of silica and other minerals that were dissolved from the core by the generated acid. Moreover, the NMR measurement did not exhibit any change in the core pore system which indicates no plugging created. As shown in Figure 7, the relaxation time (T_2) curves of the core before and after the treatment represent only one main peak. This means that the core preserved its integrity and no other pore systems were created, just the existing pores were enlarged. The major T_2 value for the fresh core was about 158 ms, while it reached more than 280 ms after acidizing treatment. This indicates that the enlargement happened to the core pore system after the in situ acid treatment.
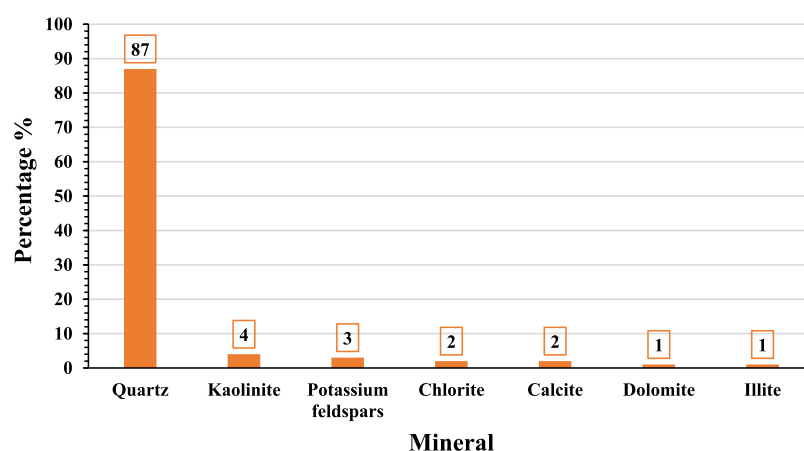
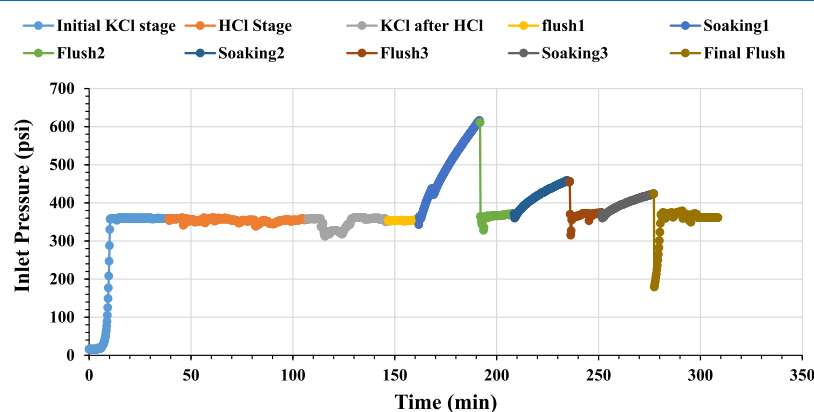**Figure 3.** Mineralogy analysis of Gray Berea sandstone cores.

Figure 4. Inlet pressure profile measured in psi during the whole treatment process of the Gray Berea sandstone core.
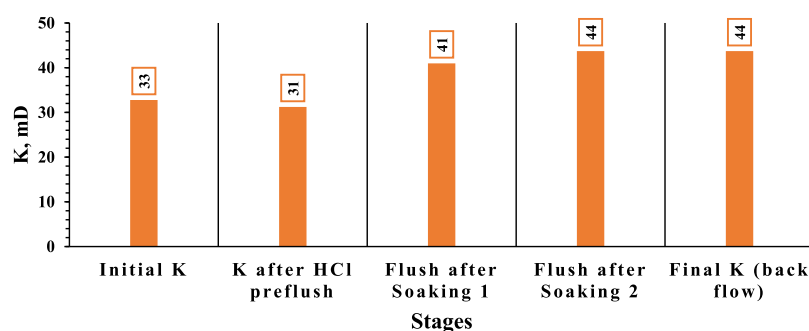

Figure 5. Core permeability values measured in mD as calculated after each treatment cycle.

Another way that can confirm the core integrity after the acidizing treatment is the results of the scratch test. These results show an enhancement in the rock mechanical parameters such as uniaxial compressive strength (UCS), sonic parameters (compressional and shear waves), and the dynamic elastic parameters (dynamic Young's modulus and Poisson's ratio). Figures 8 and 9 show the scratched cores with the groove created along the core whole length. The UCS value increased by about 1800 psi after the acid treatment as shown in Figure 10. The compressional wave velocity increased from 2471 m/s to about 3227 m/s, while the shear wave velocity increased from 1558 m/s to about 1987 m/s (Figure 11). The increase in the sonic waves is reflected by an increase in Young's modulus and Poisson's ratio by about 1400 ksi and 0.02, respectively (Figures 12 and 13).

The increase in the rock mechanical strength can be attributed to the generation of the fluoboric acid from the reaction of the excess amount of HF generated with the brome source ($NaBrO_3$) as described by eq 8.[46] The generated fluoboric acid can react with the potassium source in the Gray Berea core and form a solid precipitate of potassium tetrafluoborate (KBF_4) under high-temperature conditions. This solidification occurring inside the core is the main reason for increasing the core strength. Moreover, the heat generated from the exothermic reaction could increase the strength of sandstone samples.[47]
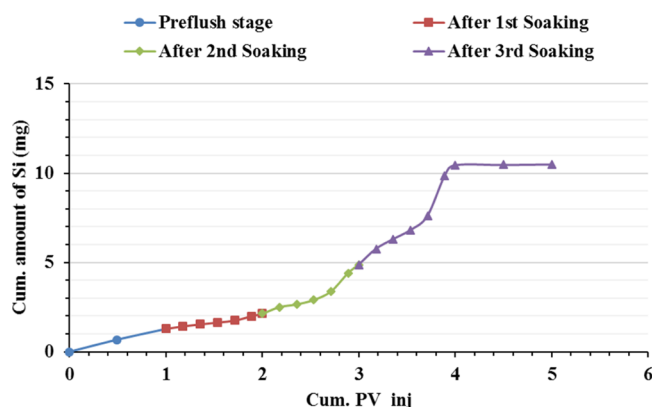
$$2NH_4HF_2 + H_3BO_3 + 2HCl$$
$$\leftrightarrow 3H_2O + HBF_4 + 2NH_4Cl \qquad (8)$$
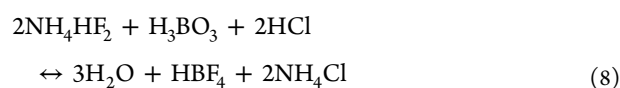
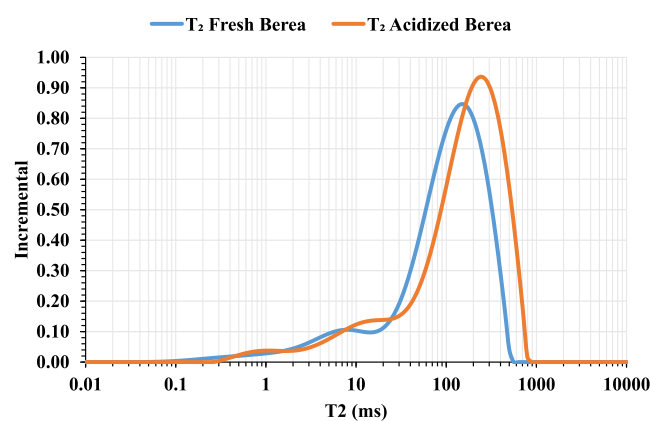**Figure 6.** Cumulative amount of Si chelated from the Gray Berea core after each treatment cycle.

Figure 7. T_2 relation time measured by the NMR technique for both fresh and acidized Gray Berea cores.

3. SUMMARY AND CONCLUSIONS

Sandstone formations have a complex mineral composition consisting of silica, calcite, feldspars, and clays. The stimulation of sandstone formation using conventional mud acid is a risky job that can increase the formation damage rather than enhancing the formation productivity. In this work, a novel approach for acidizing sandstone formations using in situ-generated HF has been developed. An acid precursor

(ammonium fluoride NH_4F) reacted with a suitable oxidizer (sodium bromates $NaBrO_3$) in an exothermic reaction. In addition, it produces a high-pressure pulse (about 600 psi) accompanied by the evolving nitrogen gas. This helps to evict any potential precipitations that may result from the acidizing treatment. The following are the main conclusions that can be drawn from this study:

- The in situ-generated HF could dissolve the silica minerals from the quartz sample.
- A Gray Berea sandstone core was successfully stimulated using core flooding. The core permeability got enhanced by about 40% with a final permeability value of 44 mD compared to an initial permeability of 31 mD.
- The ICP analysis of the core flooding effluent showed a total amount of 10.5 mg of silicon chelated from the core.
- The NMR measurement for the stimulated core before and after the treatment showed an increase in the core porosity because of the minerals dissolved.
- The scratch test results showed an enhancement in the core mechanical properties because of the solidification reaction that took place between the injected chemicals and the potassium mineral in the Berea core.
- The core UCS value increased by about 2200 psi after the acid treatment, while the dynamic Young's modulus and Poisson's ratio increased by about 1400 ksi and 0.02, respectively.

Besides the generated acid, the produced temperature and pressure will increase the acidizing process efficiency and the acid depth of penetration. This approach will, additionally, eliminate all the hazards and high safety precautions taken during the mud acid treatment. All the injected chemicals are environmentally friendly and do not cause any harm to the well.

4. RECOMMENDATIONS FOR FUTURE WORK

In order to maximize the output from this research, the following points are highly advised to be taken into consideration:

- Carrying out the core flooding tests with longer cores (1 ft or more) in order to get a representative response like that of an actual well.
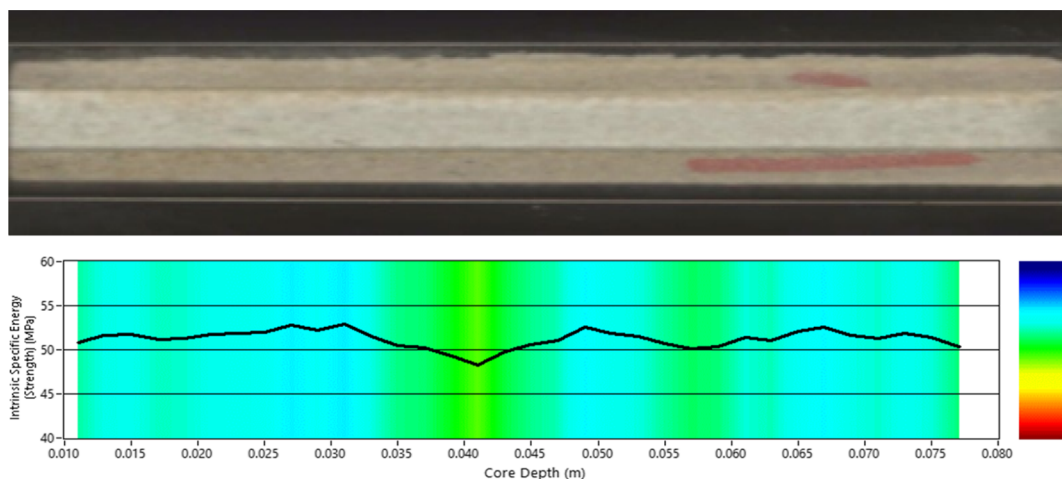

Figure 8. Groove created along the whole length of the fresh Gary Berea SS core with the recorded rock strength in MPa.
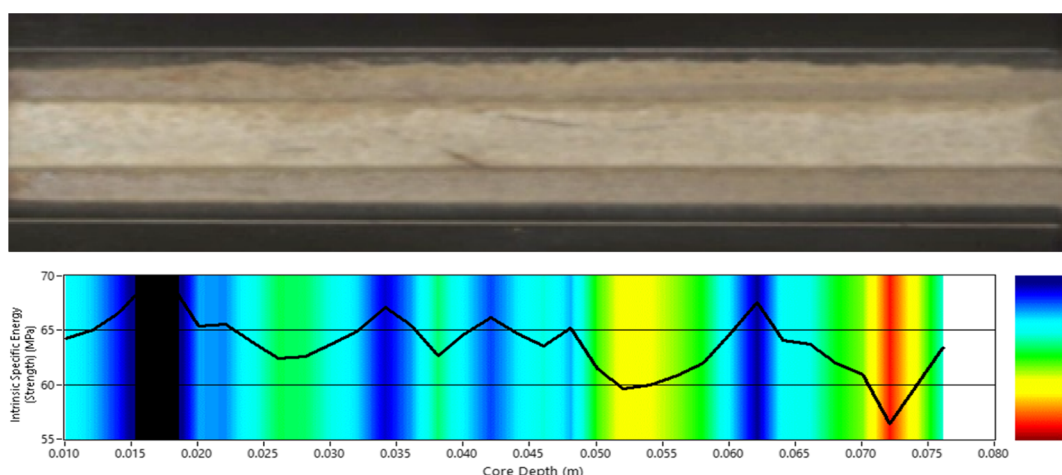
Figure 9. Groove created along the whole length of the acidized Gary Berea core with the recorded rock strength in MPa.
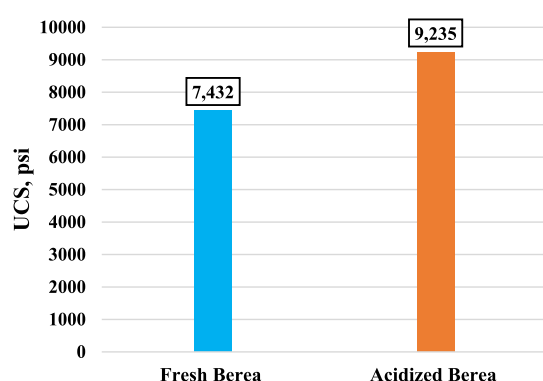

Figure 10. UCS values of the Gray Berea core measured in psi before and after the acid treatment measured by the scratch test.
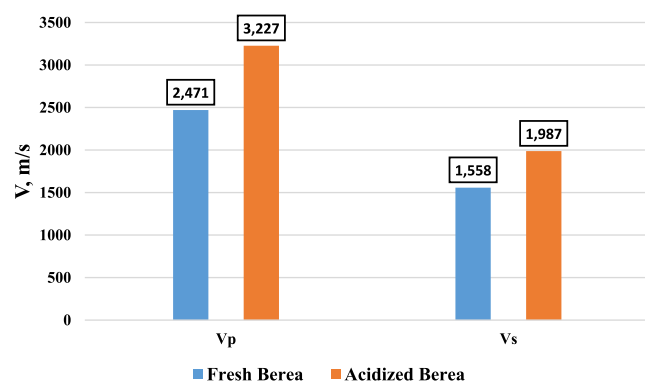

Figure 11. Compression and shear waves of the Gray Berea core measured in m/s before and after the acid treatment.

- Examining more types of sandstone formations with different quartz and clay contents to check the effect of the novel fluid mixture on them.
- Carrying out thin-section analysis for the tested sandstone cores in order to characterize the nature of their clay content and know if they will be affected with the acid flow path.

5. EXPERIMENTAL SECTION

The methodology of this research can be divided into different phases. Each phase is carried out separately in order to evaluate
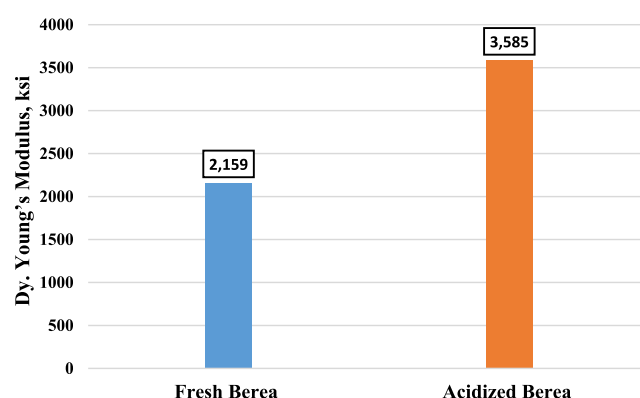

Figure 12. Dynamic Young's modulus of the Gray Berea core measured in ksi before and after the acid treatment.
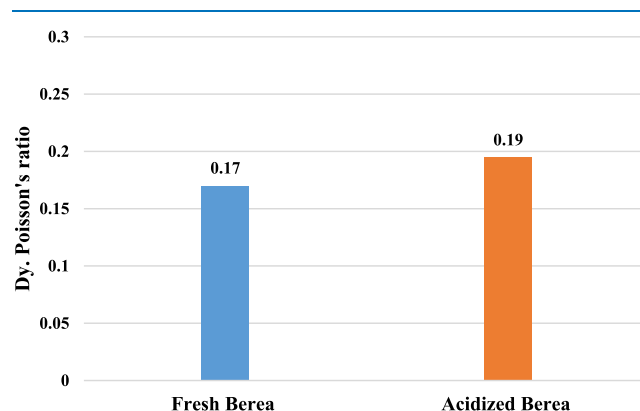

Figure 13. Dynamic Poisson's ratio of the Gray Berea core measured before and after the acid treatment.

the stated approach for generating the in situ HF and stimulating the sandstone formations.

5.1. Chemical Preparation and Quartz Dissolution. In this stage, a pure quartz sample is tested with the proposed chemical mixture to check the concept of HF generation. The pure quartz is used to avoid any reaction complication because of the impurities, clays, and feldspars that may exist in sandstone cores. The concentration of the thermochemical reactants (NH_4Cl & $NaNO_2$) is kept constant for this stage at the basis of a 1:1 molar ratio. The molar ratio of the sodium bromate to the ammonium fluoride was 1:2. The quartz

samples were weighed by using a digital balance with a high accuracy of up to 0.1 mg. Then, the samples were dispersed with the chemical mixtures in Teflon liners. The mixtures were stirred for a specific period and then kept in aging cells and placed in a digital oven for 24 h under a temperature of 90 °C (Figure 14). After that, the aging cells were removed from the

Figure 14. Aging cell with a Teflon liner (on the right) where the pure quartz samples are mixed with the chemical compounds and sealed to withstand the high pressure generated. The cell is then kept in the electrical oven (on the left) at a temperature of 90 °C for 24 h.

oven to cool down and the remaining quartz is weighed to check for any weight change while the effluent was tested by ICP-OES for the concentration of Si$^+$ ions.

5.2. Core Flooding. In this stage, core flooding was conducted using Gray Berea sandstone cores. The Gray Berea core represents sandstone formations with moderate to high permeability. The core flooding system consists of a high-pressure syringe pump used to transfer the injected fluids from three transfer cells. A sandstone core of 6 in. length and 1.5 in. diameter was placed in a core holder that is preserved in an oven. The inlet and outlet pressures of the core are continuously measured by pressure transducers that are connected to an automatic data acquisition system "OMEGA". A constant back-pressure of 366 psi is imposed on the flow system to ensure homogeneous flow within the core (Figure 15).

The sandstone treatment process had different stages. First, a solution of 3 wt % KCl is injected continuously at a constant rate until the steady-state flow is achieved. The KCl concentration was chosen based on the recommendations of Schneider[48] to increase the clay stability. For the Gray Berea core, the flow rate was set to be 2 cm^3/min. The pressure drop during this stage is used to calculate the core initial permeability using eq 9. A preflush stage of 5 PV of 7 wt % HCl is injected to dissolve any calcite content that may exist in the core. The concentration of the preflush acid was determined based on the recommendations of McLeod and Norman.[49] The core permeability is measured using the 3 wt % of KCl solution to determine the amount of damage occurred to the core after the HCl flooding stage. After that, the core is flushed by 1 PV of the main chemical mixture and left for soaking for about 30 min. There are two options to activate the exothermic chemical reaction: whether to increase the whole system temperature up to 90 °C or to inject acetic acid with pH ≤ 4. The end of the soaking period is marked by the end of the chemical reaction. The flushing and soaking cycle is repeated for 3 successive cycles. Finally, the final core permeability is measured by the backflow of the 3 wt % KCl solution. All the effluents produced during the treatment process are kept for analyzing the Si$^+$ ions using the ICP-OES system.

$$K = 122.812 \frac{q\mu L}{D^2 \Delta P} \tag{9}$$

where K is the core permeability in mD, q is the flow rate in cm^3/min, μ is the injected fluid viscosity in cP, L is the core length in inch, D is the core diameter in inch, and ΔP is the pressure drop across the core in psi.

5.3. Pore System and Core Integrity Evaluation. The pore system and rock mechanical properties are evaluated before and after the coreflooding test using the NMR technique and the scratch test. The Oxford Geospec NMR rock core analyzer is used for scanning the core with the NMR technique before and after the flooding. This version comes with an operating frequency of 2 MHz. It has two different cells, the standard one that can withstand samples of 2 in. diameter and 5 in. length. The other "P5 Overburden cell" can withstand samples of 1.5 in. diameter and 2 in. length. The maximum working pressure and temperature of this device are 5000 psi and 100 °C, respectively. The core was first saturated with brine solution, and then, the scanning process took place. The T_2 relaxation time is recorded to give an indication of the pore size distribution and the different pore size systems that may exist in the rock.

The scratch test equipment was used to assess the core mechanical property change after the stimulation treatment. The scratch test involves creating a groove on a surface of a specimen using a cutter. The test is carried out under a highly controlled kinematic process as the cutting depth and the cutter speed are highly controlled and kept constant. The
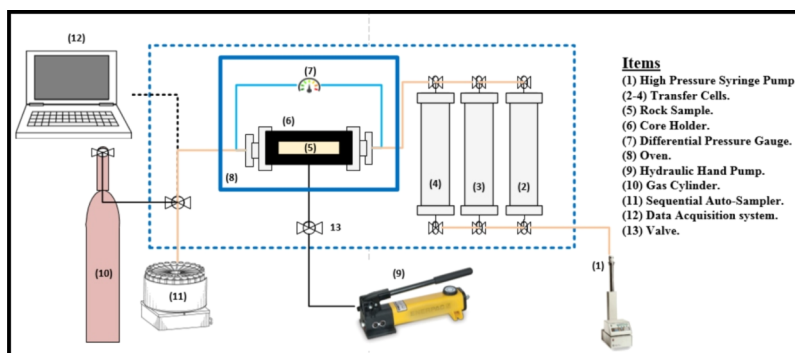

Figure 15. Core flooding system used for stimulating the Gray Berea sandstone cores.

groove depth reaches only 1 mm or less, depending on the sample strength. While scratching the sample, the force applied on the cutter is monitored and then interpreted to give an indication of the rock strength and the UCS value.[50] The test is conducted along the entire specimen length. The cutter in this test has a width of 10 mm with a back-rake angle of 15° and a velocity of 4 mm/s. By using the sonic mode in the machine, the compressional and shear waves (V_P and V_S) are measured along the sample length. The values of the sonic waves along with the rock density (ρ) can be used to calculate the dynamic elastic properties of the rock sample by using the following two eqs 10 and 11.

$$E_{dyn} = \rho V_s^2 \left(\frac{3V_p^2 - 4V_s^2}{V_p^2 - V_s^2} \right) \tag{10}$$

$$\nu_{dyn} = \frac{V_p^2 - 2V_s^2}{2(V_p^2 - V_s^2)} \tag{11}$$

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Notes

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■ REFERENCES

(1) Civan, F. Special Issue. *J. Energy Resour. Technol.* **2005**, *127*, 169−170.

(2) Amaerule, J. O.; Kersey, D. G.; Norman, D. K.; Shannon, P. M. Advances in Formation Damage Assessment and Control Strategies. *Annual Technical Meeting*; Petroleum Society of Canada, 1988.

(3) Bennion, B. Formation Damage-The Impairment of the Invisible, By the Inevitable and Uncontrollable, Resulting In an Indeterminate Reduction of the Unquantifiable! *J. Can. Pet. Technol.* **1999**, *38*, 11−17, DOI: 10.2118/99-02-DA.

(4) Economides, M. J. How to Engineer a Fracturing Treatment. *J. Pet. Technol.* **1987**, *39*, 1343−1345.

(5) Dejam, M. Tracer Dispersion in a Hydraulic Fracture with Porous Walls. *Chem. Eng. Res. Des.* **2019**, *150*, 169−178.

(6) Dejam, M.; Hassanzadeh, H.; Chen, Z. Semi-Analytical Solution for Pressure Transient Analysis of a Hydraulically Fractured Vertical Well in a Bounded Dual-Porosity Reservoir. *J. Hydrol.* **2018**, *565*, 289−301.

(7) Vogt, T. C.; Anderson, M. L. Optimizing the Profitability of Matrix Acidizing Treatments. *J. Pet. Technol.* **1974**, *26*, 1055−1062.

(8) McLeod, H. O. Matrix Acidizing. *J. Pet. Technol.* **1984**, *36*, 2055−2069.

(9) Hongjie, X. Prediction of Effective Acid Penetration and Acid Volume for Matrix Acidizing Treatments in Naturally Fractured Carbonates. *SPE Prod. Facil.* **1994**, *9*, 188−194.

(10) Zou, C.; Qin, Y.; Yan, X.; Zhou, L.; Luo, P. Study on Acidizing Effect of Cationic β-Cyclodextrin Inclusion Complex with Sandstone for Enhancing Oil Recovery. *Ind. Eng. Chem. Res.* **2014**, *53*, 12901−12910.

(11) Zakaria, A. S.; Nasr-El-Din, H. A.; Ziauddin, M. Flow of Emulsified Acid in Carbonate Rocks. *Ind. Eng. Chem. Res.* **2015**, *54*, 4190−4202.

(12) Cairns, A. J.; Hull, K. L.; Sayed, M. From Design to Practice: Development of New Acid Platforms To Address Upstream Oil and Gas Production Challenges In *Chemistry Solutions to Challenges in the Petroleum Industry*; Rahimi, P. M., Ed.; American Chemical Society, 2019; pp 3−21.

(13) Coulter, A. W. J.; Hendrickson, A. R.; Martinez, S. J. Acidizing. *Petroleum Engineering Handbook*; Society of Petroleum Engineers, 1987.

(14) Olayiwola, S. O.; Dejam, M. A Comprehensive Review on Interaction of Nanoparticles with Low Salinity Water and Surfactant for Enhanced Oil Recovery in Sandstone and Carbonate Reservoirs. *Fuel* **2019**, *241*, 1045−1057.

(15) Leong, V. H.; Ben Mahmud, H. A Preliminary Screening and Characterization of Suitable Acids for Sandstone Matrix Acidizing Technique: A Comprehensive Review. *J. Pet. Explor. Prod. Technol.* **2019**, *9*, 753−778.

(16) Economides, M. J.; Hill, A. D.; Ehlig-Economides, C.; Ding, Z. *Petroleum Production Systems*, 2nd ed.; Prentice Hall: Upper Saddle River, NJ, 2013.

(17) McCune, C. C.; Fogler, H. S.; Kline, W. E. An Experimental Technique for Obtaining Permeability-Porosity Relationships in Acidized Porous Media. *Ind. Eng. Chem. Fundam.* **1979**, *18*, 188−191.

(18) Kume, N.; Van Melsen, R.; Erhahon, L.; Abiodun, A. F. New HF Acid System Improves Sandstone Matrix Acidizing Success Ratio By 400% Over Conventional Mud Acid System in Niger Delta Basin. In *SPE Annual Technical Conference and Exhibition*, 1999.

(19) Hartman, R. L.; Fogler, H. S. Reaction kinetics and mechanisms of zeolite dissolution in hydrochloric acid. *Ind. Eng. Chem. Res.* **2005**, *44*, 7738−7745.

(20) Nevito Gomez, J. Design, set up, and testing of a matrix acidizing apparatus. M.Sc Thesis, Texas A&M University, 2006. http://hdl.handle.net/1969.1/4282.

(21) Sutton, G. D.; Lasater, R. M. Aspects of Acid Additive Selection in Sandstone Acidizing. In *Fall Meeting of the Society of Petroleum Engineers of AIME*, 1972.

(22) Gidley, J. L.; Brezovec, E. J.; King, G. E. An Improved Method for Acidizing Oil Wells in Sandstone Formations. *SPE Prod. Facil.* **1996**, *11*, 4−10.

(23) Shafiq, M. U.; Mahmud, H. B. Sandstone Matrix Acidizing Knowledge and Future Development. *J. Pet. Explor. Prod. Technol.* **2017**, *7*, 1205−1216.

(24) Al-Shaalan, T. M.; Nasr-El-Din, H. A. Mathematical Modeling of Sandstone Stimulation: A Critical Review of Available Models. *Corrosion 2000*; NACE International, 2000. https://www.onepetro.org/conference-paper/NACE-00443.

(25) Li, N.; Zeng, F. B.; Li, J.; Zhang, Q.; Feng, Y.; Liu, P. Kinetic Mechanics of the Reactions between HCl/HF Acid Mixtures and Sandstone Minerals. *J. Nat. Gas Sci. Eng.* **2016**, *34*, 792−802.

(26) Mahmoud, M. A.; Nasr-El-Din, H. A.; De Wolf, C. A. High-Temperature Laboratory Testing of Illitic Sandstone Outcrop Cores With HCl-Alternative Fluids. *SPE Prod. Oper.* **2015**, *30*, 43−51.

(27) Malate, R. C. M.; Austria, J. J. C.; Sarmiento, Z. F.; Di Lullo, G.; Sookprasong, P. A.; Francis, E. S. Matrix Stimulation Treatment of Geothermal Wells Using Sandstone Acid. *Proceedings of the Twenty-Third Workshop on Geothermal Reservoir Engineering*; Stanford University: Stanford, California, 1998.

(28) Portier, S.; André, L.; Vuataz, F. Review on Chemical Stimulation Techniques in Oil Industry and Applications to Geothermal Systems. Presented at the *Enhanced Geothermal Innovative Network for Europe*; Deep Heat Mining Association—DHMA: Switzerland, 2007.

(29) Al-Dahlan, M. N.; Nasr-El-Din, H. A.; Al-Qahtani, A. A. Evaluation of Retarded HF Acid Systems. In *SPE International Symposium on Oilfield Chemistry*, 2001.

(30) McCune, C. C.; Fogler, H. S.; Cunningham, J. R. A New Model of the Physical and Chemical Changes in Sandstone During Acidizing. *Soc. Pet. Eng. J.* **1975**, *15*, 361−370.

(31) Hill, A. D.; Lindsay, D. M.; Silberberg, I. H.; Schechter, R. S. Theoretical and Experimental Studies of Sandstone Acidizing. *Soc. Pet. Eng. J.* **1981**, *21*, 30−42.

(32) Li, Y.-H.; Fambrough, J. D.; Montgomery, C. T. Mathematical Modeling of Secondary Precipitation From Sandstone Acidizing. *Soc. Pet. Eng. J.* **1998**, *3*, 393−401.

(33) Templeton, C. C.; Richardson, E. A.; Karnes, G. T.; Lybarger, J. H. Self-Generating Mud Acid. *J. Pet. Technol.* **1975**, *27*, 1199−1203.

(34) Chang, F.; Thomas, R. L.; Grant, W. D., Jr. Method for acidizing a subterranean formation; World Intellectual Property Organization, WO2000070186A1, Nov 23, 2000.

(35) Gdanski, R. D. AlCl₃ Retarded HF Acid for More Effective Stimulation. *Oil Gas J.* **1985**, *83*, 111−115.

(36) Ayorinde, A.; Granger, C.; Thomas, R. L. The Application of Fluoboric Acid in Sandstone Matrix Acidizing. A Case Study. *21st Annual Convention Proceedings*, 1992; Vol. 2, pp 235−261. http://archives.datapages.com/data/ipa/data/021/021002/235_ipa021b0235.htm.

(37) Rogers, B. A.; Burk, M. K.; Stonecipher, S. A. Designing a Remedial Acid Treatment for Gulf of Mexico Deepwater Turbidite Sands Containing Zeolite Cement. In *SPE Formation Damage Control Conference*, 1998.

(38) Al-Harbi, B. G.; Al-Khaldi, M. H.; Al-Dahlan, M. N. Evaluation of Chelating-Hydrofluoric Systems. In *International Petroleum Technology Conference*, 2013.

(39) Li, N.; Zhang, Q.; Wang, Y.; Liu, P.; Zhao, L. A New Multichelating Acid System for High-Temperature Sandstone Reservoirs. *J. Chem.* **2015**, *2015*, 1−9.

(40) Karale, C. M.; Salla, R.; Poyyara, R. L. A Method Of Acidizing Subterranean Formations in Well Operations. WO2016126351A1, Aug 11, 2016. https://patentscope.wipo.int/search/en/detail.jsf?docId=WO2016126351.

(41) Al-Nakhli, A. R.; Sukkar, L. A.; Arukhe, J.; Mulhem, A.; Mohannad, A.; Ayub, M.; Arifin, M. In-Situ Steam Generation a New Technology Application for Heavy Oil Production. *SPE Heavy Oil Conference and Exhibition*, 2016.

(42) Alade, O. S.; Mahmoud, M.; Hassan, A.; Al-Shehri, D.; Al-Nakhli, A.; Bataweel, M. Evaluation of Kinetics and Energetics of Thermochemical Fluids for Enhanced Recovery of Heavy Oil and Liquid Condensate. *Energy Fuels* **2019**, *33*, 5538−5543.

(43) Hull, K. L.; Cairns, A. J.; Haq, M. Bromate Oxidation of Ammonium Salts: In Situ Acid Formation for Reservoir Stimulation. *Inorg. Chem.* **2019**, *58*, 3007−3014.

(44) Thomas, R. L.; Nasr-El-Din, H. A.; Lynn, J. D.; Mehta, S.; Zaidi, S. R. Precipitation During the Acidizing of a HT/HP Illitic Sandstone Reservoir in Eastern Saudi Arabia: A Laboratory Study. In *SPE Annual Technical Conference and Exhibition*, 2001.

(45) Kamal, M. S.; Mahmoud, M.; Hanfi, M.; Elkatatny, S.; Hussein, I. Clay Minerals Damage Quantification in Sandstone Rocks Using Core Flooding and NMR. *J. Pet. Explor. Prod. Technol.* **2019**, *9*, 593−603.

(46) Pituckchon, A. Further Investigation of Fluoboric Acid in Sandstone Acidizing Using ¹¹B And ¹⁹F NMR. M.Sc Thesis, Texas A&M University, 2014.

(47) Sygała, A.; Bukowska, M.; Janoszek, T. High Temperature Versus Geomechanical Parameters of Selected Rocks − The Present State of Research. *J. Sustain. Min.* **2013**, *12*, 45−51.

(48) Schneider, G. W. A Geochemical Model of the Solution-Mineral Equilibria within a Sandstone Reservoir. M.Sc. Thesis, The University of Oklahoma, 1997; p 157.

(49) McLeod, H. O., Jr.; Norman, W. D. Sandstone Acidizing. In *Reservoir Stimulation*, 3rd ed.; Economides, M. J., Nolte, K. G., Eds.; John Wiley and Sons: Chichester, UK, 2000; Chapter 18.

(50) Richard, T.; Dagrain, F.; Poyol, E.; Detournay, E. Rock Strength Determination from Scratch Tests. *Eng. Geol.* **2012**, *147−148*, 91−100.